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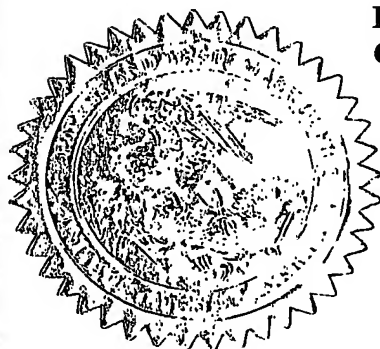
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Yodh Islam	Arjun Mohammad	G F	Merion, PA Philadelphia, PA
Title of the Invention (280 Characters Maximum)			
High Weight-fraction Surfactant Selfubilization of Single-wall Carbon Nanotubes in Water			
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Respectfully submitted,

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☐ Additional inventors are being named on separately numbered sheets attached hereto.

**PROVISIONAL APPLICATION FILING ONLY**

# High weight-fraction surfactant solubilization of single-wall carbon nanotubes in water

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(Dated: September 5, 2002)

Most applications employing the unique properties of individual single-wall carbon nanotubes (SWNTs) [1–4] will require large-scale manipulation of stable suspensions at high weight-fraction. Tube solubilization provides access to solution-phase separation methodologies [5, 6], and facilitates chemical derivatization [7], controlled dispersion and deposition [8], microfluidics, fabrication of nanotube-based fibers [9] and composites [10], and optical diagnostics [11]. Furthermore, high volume-fraction suspensions will bring nanotube science into better contact with fundamental research on self-assembly in complex fluids [12–14]. Thus far, some limited progress has been made towards solubilization of SWNTs in organic [15, 16] and aqueous media. Dissolution in water, important because of potential biomedical applications and biophysical processing schemes, has been facilitated by surfactants [5, 17], by polymer wrapping [18, 19], and by more perturbative chemical modification [20, 21]. We have discovered that a novel surfactant, sodium dodecylbenzene sulfonate (NaDDBS), consisting of a benzene ring moiety, a charged head group, and an alkyl chain, enhances the stability of SWNTs in water by  $\sim 100$  compared to other commonly employed surfactants. A single step solubilization scheme was developed, mixing nanotubes with surfactants in low-power high-frequency sonicators for long time periods; the scheme enhanced disaggregation of bundles with dramatically less tube breakage. New insight about nanotube solubilization is derived from comparisons of SWNT yield as a function of surfactant type, concentration, and sonication procedure, using tube diameter and length distributions measured by atomic force microscopy (AFM).

In order to evaluate competing stabilization characteristics, we explored the dispersing power of a range of surfactants: NaDDBS ( $C_{12}H_{25}C_6H_4SO_3Na$ ), sodium octylbenzene sulfonate (NaOBS;  $C_8H_{17}C_6H_4SO_3Na$ ), sodium butylbenzene sulfonate (NaBBS;  $C_4H_9C_6H_4SO_3Na$ ), sodium benzoate ( $C_6H_5CO_2Na$ ), sodium dodecyl sulfate (SDS;  $CH_3(CH_2)_{11}OSO_3Na$ ), Triton X-100 (TX100;  $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$ ;  $n \sim 10$ ), dodecyltrimethylammonium bromide (DTAB;  $CH_3(CH_2)_{11}N(CH_3)_3Br$ ), Dextrin, and poly(styrene)-poly(ethylene oxide) (PS-PEO) diblock copolymer.

The NaDDBS-nanotube dispersions, and one close relative, were by far the most stable; dispersed nanotube

concentrations ranged from 0.1 mg/ml to 20 mg/ml. The resulting suspensions remained dispersed for at least three months; neither sedimentation nor aggregation of nanotube bundles was observed in these samples. By contrast we were unable to prepare stable nanotube suspensions with the other additives at concentrations greater than 0.5 mg/ml. With the exception of NaOBS, a close relative of NaDDBS, reliable disaggregated dispersions in the other surfactants required nanotube concentrations of  $\sim 0.1$  mg/ml.

Figure 1(a) exhibits vials of the nanotube dispersions in NaDDBS at 20 mg/ml, in SDS at 0.5 mg/ml, and in TX100 at 0.8 mg/ml. We readily observe the NaDDBS-nanotube dispersion is homogeneous, whereas SDS-nanotube and TX100-nanotube dispersions contain coagulated bundles of tubes at the bottom of their respective vials. Quantitative information about the distribution of the diameter and length of the dispersed nanotubes was derived directly by AFM. An example of an AFM image used for the analysis is shown in Figure 1(b).

A summary of the AFM observations is given in Figure 2. We examined  $\sim 300$  tubes for each distribution plot. The shaded regions define single tubes; we assumed 1.3 and 1.5 nm respectively, as the upper bound for a single tube diameter of HiPCO [22] and of laser-oven [23] nanotubes respectively. The first four distributions are for NaDDBS-HiPCO dispersions. From Figure 2(a) we see that a NaDDBS-HiPCO dispersion prepared at 0.1 mg/ml was  $\sim 74 \pm 5\%$  single tubes. This yield changed modestly as a function of increasing nanotube weight-fraction, see Figure 2(b) and Figure 2(c). Furthermore, we measured the distribution from the 10 mg/ml suspension after allowing it to sit for one month, the single-tube fraction did not change appreciably ( $\sim 54 \pm 5\%$ ; Figure 2(d)). By contrast, HiPCO stabilized in SDS and TX100 at a concentration of just 0.1 mg/ml had SWNT yields of only  $\sim 16 \pm 2\%$  (Figure 2(e)) and  $\sim 36 \pm 3\%$  (Figure 2(f)), respectively.

The mean length ( $L_{\text{mean}}$ ) of single tubes for the four NaDDBS-HiPCO distributions was  $\sim 165$  nm with a standard deviation between 75 and 95 nm. The number of longer tubes (i.e.,  $\geq 300$  nm) was observed to decrease slightly in the samples that were diluted to 1 mg/ml (distributions not shown). SWNT length distributions for SDS-HiPCO ( $L_{\text{mean}} \sim 105$  nm  $\pm 78$  nm), and for TX100-HiPCO ( $L_{\text{mean}} \sim 112$  nm  $\pm 54$  nm) were shifted a bit lower; generally we did not find many long SWNTs using SDS or TX100.

We now return to consider the solubilizing capabilities of the various surfactants. Any successful method must

reckon with the substantial van der Waals attractions of bare tubes [24]. A schematic of how our surfactants might adsorb onto the nanotubes is suggested in Figure 3; we believe the tubes are stabilized by hemi-micelles [25–27] that sheath the surface. The superior dispersing capability of NaDDBS compared to SDS (dispersing capability,  $\leq 0.1$  mg/ml) or TX100 ( $\leq 0.5$  mg/ml) can be explained in terms of graphite-surfactant interactions, alkyl chain length, head group size and charge as pertains particularly to those molecules that lie along the surface, parallel to the tube central axis. We suspect SDS has a weaker interaction with the nanotube surface compared to NaDDBS and TX100, because it does not have a benzene ring. Indeed  $\pi$ -like stacking of the benzene rings onto the surface of graphite is believed to significantly increase the binding and surface coverage of surfactant molecules to graphite [27]. Dextrin ( $< 0.05$  mg/ml) and DTAB ( $< 0.1$  mg/ml) also did not disperse nanotubes well because, we believe, they do not have ring moieties.

We suspect the alkyl chain part of surfactant molecules to lie flat on the graphite surface, [25–27]. Most of our surfactants had alkyl chains with lengths of order 2 nm. Thus, when adsorbing onto a small diameter nanotube surface it is probably energetically favorable for the chains to lie along the length of the nanotubes rather than bend around the circumference. This chain interaction distinguishes TX100 (8 carbon alkyl chain) from NaDDBS and SDS (both have 12 carbon alkyl chain). Longer chain lengths improve surfactant energetics, given similar ring and head groups. For example, sodium benzoate (no alkyl chain,  $\leq 0.01$  mg/ml), and NaBBS (4 carbon alkyl chain,  $< 0.1$  mg/ml) have same ring and headgroup size as NaDDBS, but performed relatively poorly because of substantially shorter alkyl chain length. On the other hand, NaOBS (8 carbon alkyl chain,  $\leq 8$  mg/ml) performed quite well. Sodium hexadecylbenzene sulfonate had a longer alkyl chain (16 carbon), but did not dissolve in water at high concentration ( $\geq 5$  wt%) at room temperature.

The different-responses of NaDDBS and TX100 probably arise from head group and chain lengths. The head group of TX100 (PEO chains) is polar and larger than NaDDBS ( $\text{SO}_3^-$ ); its large size may lower its packing density compared to NaDDBS. Furthermore, the electrostatic repulsion of  $\text{SO}_3^-$  leads to charge stabilization of tubes via screened Coulomb interactions which, in analogy with colloidal particle stabilization, may be significant for solubilization in water compared to the more steric repulsion of the TX100 head group. Generally, added salt (NaCl) of greater than 25 mM induced aggregation in the NaDDBS samples. PS-PEO diblocks, which had long PEO chains as headgroup, did not stabilize nanotubes well ( $\leq 0.1$  mg/ml).

Lastly, we investigated the relative efficacy of different sonication techniques on the dispersion of nanotubes. Tube breakage is a critical parameter; SWNTs with large lengths (e.g.,  $> 500$  nm) are often preferred because, for example, they introduce greater anisotropies into the

properties of composites [28]. The standard approach is to disperse nanotubes using a high power tip sonicator (1/8 in, 6 W, 22.5 KHz) for short time ( $\sim 1$  hour). For comparison we prepared 0.1 mg/ml of HiPCO and laser-oven tubes in NaDDBS, SDS and TX100, and computed length and diameter distributions. The essential observations are summarized in Figure 4 for 0.1 mg/ml laser-oven tubes in NaDDBS. The nanotube dispersion prepared by bath sonication had very high yield of single tubes ( $\sim 90 \pm 5\%$ ), a significant fraction of which were long single tubes with lengths larger than 400nm ( $L_{\text{mean}} \sim 516$  nm  $\pm 286$  nm), see Figure 4(a). Similar samples prepared by tip sonication (Figure 4(b)) had lower SWNT yield ( $\sim 50 \pm 4\%$ ), and  $L_{\text{mean}} \sim 267$  nm  $\pm 126$  nm. These effects were not as pronounced in HiPCO samples, because the nanotubes were already rather short.

To summarize, we have demonstrated a simple scheme to solubilize high weight-fraction single-wall carbon nanotubes in water. Suspension concentrations were improved by approximately one hundred with respect to commonly used surfactants, and the new sonication technique also dramatically reduced tube fragmentation. Preliminary transport measurements on these tubes suggest that our treatment does not alter the SWNT electronic properties. Single tubes prepared by these means in high concentration can now be used for creation of novel composite materials, for self-assembly of tubes in suspension, and for use as sensors in water.

**Methods** Our nanotubes were obtained in purified form from Tubes@Rice (laser-oven SWNTs, batch P081600 [29]) and Carbon Nanotechnologies Inc. (HiPCO SWNTs, batch 79 [23]). The purified laser-oven nanotubes were  $> 90$  wt% SWNTs and the HiPCO samples were 99 wt% SWNTs (0.5 wt% Fe catalyst). Typically we mixed the base material with surfactant and sonicated the suspension in a low-power, high-frequency (12 W, 55 kHz) bath sonicator for  $\sim 16$  to 24 hours.

The first step towards solubilization was to find suitable concentration ratios of nanotube-to-surfactant. To this end we mixed 0.01 mg/ml nanotube dispersions with various surfactant concentrations and sonicated the suspension for 24 hours. A ratio was deemed suitable when the nanotubes dispersed and did not re-aggregate after sonication. The optimum surfactant-dependent ratio of nanotube-to-surfactant varied from 1 : 5 to 1 : 10 by weight. The optimum ratio for NaDDBS was 1 : 10. For nanotube dispersions greater than 0.1 mg/ml, the input surfactant concentration usually exceeded critical micelle concentrations (CMCs); we did not, however, observe evidence of surfactant micelles or other phases. Presumably, most surfactant in suspension adsorbed onto the nanotube surfaces [25, 26].

To obtain the AFM images and distributions we deposited surfactant-stabilized nanotubes onto a silicon wafer. The tube surface density was sufficient for analysis when the nanotube suspension weight fractions were  $\leq 1.0$  mg/ml; suspensions with greater weight fractions,

e.g. 20.0 or 10 mg/ml, were rapidly diluted to 1.0 mg/ml or 0.1 mg/ml and then spread over the silicon wafer for the AFM measurements. The AFM image quality was improved substantially by baking the resultant wafers at 180° C for ~ 4 hours; apparently baking removes much of the surfactant from the wafer and tubes. AFM images were taken in tapping mode using a Nanoscope III Multimode (Digital Instruments Inc., Santa Barbara,

CA). Digital Instrument supplied software was used to derive the length and the diameter of every accessible nanotube. Tube diameters were derived from our height measurements, which had a resolution of 0.1 nm. Tube lengths were determined within our lateral resolution of 20 – 50 nm; it was difficult to accurately characterize tubes whose lengths were less than 50 nm, so their contributions were omitted from the measured distributions.

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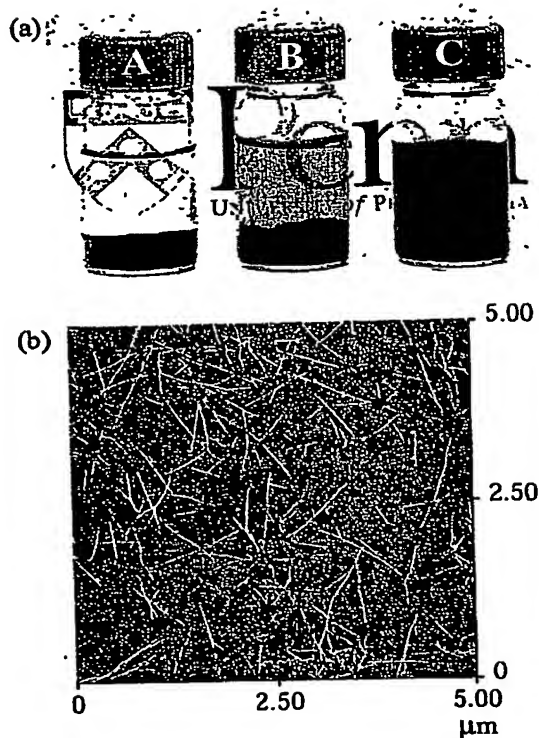


FIG. 1: (a) Vials containing aqueous dispersions of (A) SDS-HiPCO at 0.5 mg/ml, (B) TX100-HiPCO at 0.8 mg/ml; (C) NaDDBS-HiPCO of SWNTs at 20 mg/ml after 1 day at room temperature. NaDDBS-HiPCO suspensions appeared homogeneous whereas SDS-HiPCO or TX100-HiPCO suspensions had coagulated nanotubes in the body and at the bottom of the vials. (b) Tapping mode AFM image of TX100 stabilized laser-oven produced single-walled carbon nanotubes on a silicon surface. The nanotube suspension was prepared at 0.1 mg/ml by the bath sonicator.

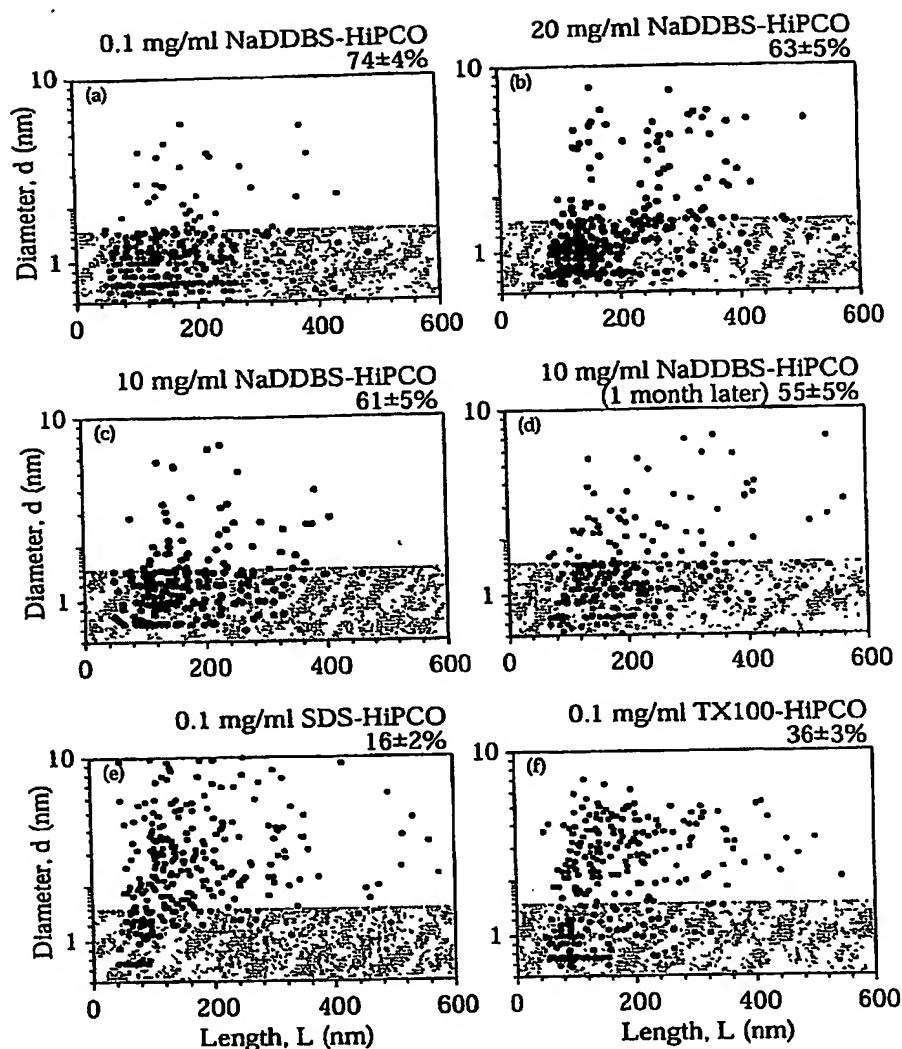


FIG 2 Length and diameter distribution of HiPCO tubes, obtained from AFM images, after dispersed by bath sonicator and stabilized by 3 different surfactants. For the sake of uniformity, the distributions were obtained by diluting the nanotube dispersions to 0.1 mg/ml (i.e. when the original suspension concentration was greater than 0.1 mg/ml). (a) The fraction of single tubes in a NaDDBS-HiPCO solution prepared at 0.1 mg/ml was  $\sim 74 \pm 5\%$ . (b) We obtained  $\sim 63 \pm 5\%$  single tubes when we prepared NaDDBS-HiPCO solution at 20 mg/ml. (c) A NaDDBS-HiPCO solution prepared at 10 mg/ml had  $\sim 61 \pm 5\%$  single tubes. (d) The distribution did not change appreciably when we looked at the sample after a month ( $\sim 55 \pm 5\%$  single tubes). When we prepared 0.1 mg/ml HiPCO solution with SDS or TritonX-100 surfactant, the fraction of single tubes were  $16 \pm 2\%$  (d) and  $36 \pm 3\%$  (e), respectively.

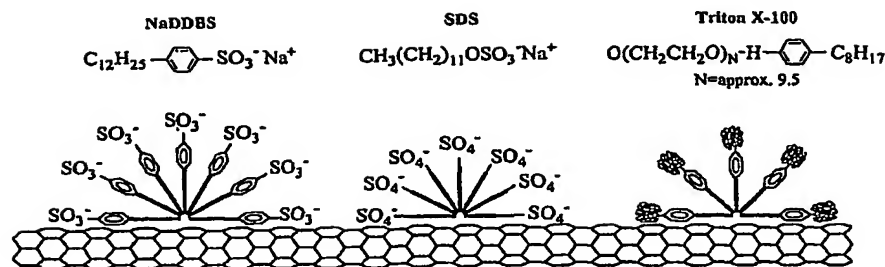


FIG 3: A schematic representation of how surfactant may adsorb onto the nanotube surface. We speculate that the alkyl chain groups of a surfactant molecule adsorb flat along the length of the tube instead of the diameter. NaDDBS and TX100 disperse the tubes better than SDS because of their benzene rings. NaDDBS disperses better than TX100 because of the head group and slightly longer alkyl chain. (see text).

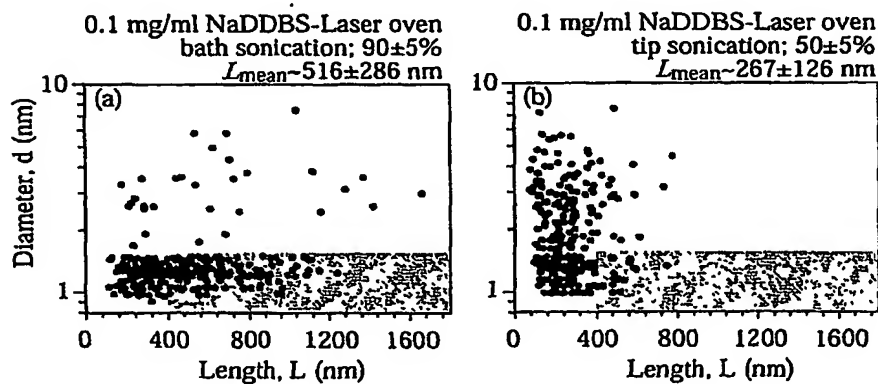


FIG 4: Length and diameter distribution of 0.1 mg/ml laser-oven single-walled nanotube suspension dispersed by tip and bath sonicators and stabilized by NaDDBS. (a) The low-power bath sonication scheme made high yield single tubes ( $90 \pm 5\%$ ) and left many single tubes with lengths larger than 400 nm.  $L_{\text{mean}}$  was  $\sim 516 \pm 286 \text{ nm}$ . (b) The tip-sonication technique gave significantly lower yield ( $50 \pm 5\%$ ) and also fragmented the tubes. We observe only a few nanotubes with lengths larger than 400 nm,  $L_{\text{mean}}$  was  $\sim 267 \pm 126 \text{ nm}$ .



# High weight-fraction surfactant solubilization of single-wall carbon nanotubes in water

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## Abstract

We have developed simple scheme to solubilize high weight-fraction single-wall carbon nanotubes (SWNTs) in water. We have discovered that a novel surfactant, sodium dodecylbenzene sulfonate (NaDDBS), consisting of a benzene ring moiety, a charged group, and an alkyl chain, dramatically enhances the stability of SWNTs in aqueous suspension compared to commonly used surfactants, e.g. sodium dodecyl sulfate (SDS) and Triton X-100 (TX100); suspension concentrations were improved by approximately one hundred with respect to commonly used surfactants. Our suspending technique is also new, eliminating high power tip- or horn-sonication and repeated centrifugation and decanting. It is a single step process, mixing SWNTs with surfactants in a low-power, high-frequency sonicator for a very long time period. This sonication procedure enhances disaggregation of bundles with dramatically less tube breakage. Diameter distributions of nanotube dispersions at the highest concentration (i.e., 20 mg/ml), measured by AFM, show that a large percentage of these nanotubes were SWNTs ( $\sim 61 \pm 3\%$ ). Initial electronic measurements show that our treatment does not alter the electronic properties of the nanotubes. Single tubes prepared by these means in high concentration can now be used for creation of novel composite materials, for self-assembly of tubes on surfaces and in suspension, and for use as chemical and bio-sensors in water.

## I. BACKGROUND

Although the novel electronic, thermal and mechanical properties of individual single-wall carbon nanotubes (SWNTs) are fascinating [1–5], most applications of SWNTs will require large-scale manipulations of stable suspensions at high weight-fraction. Tube solubilization provides access to solution-phase purification and separation methodologies [6–9], and facilitates chemical derivatization [10], controlled dispersion and deposition [11, 12], microfluidics, fabrication of nanotube-based fibers [13] and composites [14] and optical diagnostics [15]. Furthermore, high volume-fraction tube solubilization will bring nanotube science into better contact with fundamental research on interactions and self-assembly in complex fluids [16, 17]. Unfortunately nanotubes aggregate easily and are difficult to suspend as a result of substantial van der Waals attractions [18].

Thus far, some progress has been made towards solubilization of SWNTs in both organic and aqueous media. Dissolution in organic solvents has been reported with bare SWNT fragments (e.g. 100 – 300 nm in length) [19, 20], and with chemically modified SWNTs [21] [10]. Dissolution in water, important because of potential biomedical applications and biophysical processing schemes, has been facilitated by surfactants [8, 22–24] (with SDS, the most widely used surfactant), by polymer wrapping [25, 26], and by chemical modification [27–29]. Generally, the chemically modified tubes are less desirable because their band structures can differ from the bare tubes, and SWNTs with large lengths (e.g., > 500 nm) are often preferred because, for example, they introduce greater anisotropies into the properties of composites [30].

## II. DESCRIPTION OF TECHNOLOGY

Our nanotubes were obtained in purified form from Carbon Nanotechnologies Inc. (HiPCO SWNTs, batch 79 [31–33]) and Tubes@Rice (laser-oven SWNTs, batch P081600 [34]). According to manufacturer specifications, the HiPCO samples were 99 wt% SWNTs (0.5 wt% Fe catalyst) and the purified laser-oven nanotubes were > 90 wt% SWNTs. Typically we mixed the base material with surfactant and sonicated the suspension in a low-power, high-frequency (12 W, 55 kHz) bath sonicator for ~ 16 to 24 hours.

In order to evaluate competing stabilization characteristics, we explored the dis-

persing power of a range of surfactants: NaDDBS ( $C_{12}H_{25}C_6H_4SO_3Na$ ), sodium octylbenzene sulfonate (NaOBS;  $C_8H_{17}C_6H_4SO_3Na$ ), sodium butylbenzene sulfonate (NaBBS;  $C_4H_9C_6H_4SO_3Na$ ), sodium benzoate ( $C_6H_5CO_2Na$ ), sodium dodecyl sulfate (SDS;  $CH_3(CH_2)_{11}OSO_3Na$ ), Triton X-100 (TX100;  $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$ ;  $n \sim 10$ ), dodecyltrimethylammonium bromide (DTAB;  $CH_3(CH_2)_{11}N(CH_3)_3Br$ ), Dextrin, and poly(styrene)-poly(ethylene oxide) (PS-PEO) diblock copolymer.

The NaDDBS-nanotube dispersions, and one close relative, were by far the most stable; dispersed nanotube concentrations in NaDDBS ranged from 0.1 mg/ml to 20 mg/ml. The resulting suspensions remained dispersed for at least three months; neither sedimentation nor aggregation of nanotube bundles was observed in these samples. By contrast we were unable to prepare stable nanotube suspensions with the other additives at concentrations greater than 0.5 mg/ml. With the exception of NaOBS, a close relative of NaDDBS, reliable disaggregated dispersions in the other surfactants required nanotube concentrations of  $\sim 0.1$  mg/ml.

Figure 1 contains images of the nanotube dispersions in NaDDBS, SDS, and TX100 at 5 mg/ml. The NaDDBS-nanotube dispersion is homogeneous whereas SDS-nanotube and TX100-nanotube dispersions present coagulated bundles of tubes at the bottom of their respective vials. More quantitative information about the distribution of the diameter and length of the dispersed nanotubes was derived directly by atomic force microscopy (AFM).

An example of an AFM image used for the analysis, in this case of laser-oven nanotubes at a concentration of 0.1 mg/ml and stabilized by TX100, is shown in Figure 2. Typically we deposited surfactant stabilized nanotubes onto a silicon wafer. The tube surface density was sufficient for analysis when the suspension nanotube weight fractions were  $\leq 1.0$  mg/ml; suspensions with greater weight fractions, e.g. 20.0 mg/ml were rapidly diluted to 1.0 mg/ml or 0.1 mg/ml and then spread over the silicon wafer for the AFM measurements. The AFM image quality was substantially improved by baking the resultant wafers at  $180^\circ C$  for approximately 4 hours (or longer); apparently baking removes much of the surfactant from the wafer and from the tubes. AFM images were taken in tapping mode using a Nanoscope III Multimode (Digital Instruments Inc., Santa Barbara, CA). Digital Instrument supplied software was then used to derive the length and the diameter of the every accessible nanotube in the image. We excluded tubes those were not entirely within an image. Tube diameters were derived from our height measurements, which had a resolution of 0.1 nm; typically

A summary of the AFM observations is given in Figure 3. We examined  $\sim 300$  tubes for each distribution plot. The shaded regions define single tubes; we assumed 1.3 and 1.5 nm, as the upper bound for a single tube diameter of HiPCO [32] and of laser-oven [31] nanotubes, respectively. The first four distributions are for NaDDBS-HiPCO dispersions. From Figure 3(a) we see that a NaDDBS-HiPCO dispersion prepared at 0.1 mg/ml was  $\sim 74 \pm 5\%$  single tubes. This yield changed modestly as a function of increasing nanotube weight-fraction, see Figure 3(b) and Figure 3(c). Furthermore, we measured the distribution from the 10 mg/ml suspension after allowing it to sit for one month; the single-tube fraction did not change appreciably ( $\sim 54 \pm 5\%$ ; Figure 3(d)). By contrast, HiPCO stabilized in SDS and TX100 at a concentration of just 0.1 mg/ml had SWNT yields of only  $\sim 16 \pm 2\%$  (Figure 3(e)) and  $\sim 36 \pm 3\%$  (Figure 3(f)), respectively.

The mean length ( $L_{\text{mean}}$ ) of single tubes for the four NaDDBS-HiPCO distributions was  $\sim 165$  nm with a standard deviation between 75 and 95 nm. The number of longer tubes (i.e.,  $\geq 300$  nm) was observed to decrease slightly in the samples that were diluted to 1 mg/ml (distributions not shown). SWNT length distributions for SDS-HiPCO ( $L_{\text{mean}} \sim 105$  nm  $\pm 78$  nm), and for TX100-HiPCO ( $L_{\text{mean}} \sim 112$  nm  $\pm 54$  nm) were shifted a bit lower; generally we did not find many long SWNTs using SDS or TX100.

We now return to the solubilizing capabilities of the various surfactants. Any successful method must reckon with the substantial van der Waals attractions of bare tubes [18]. A schematic of how our surfactants might adsorb onto the nanotubes is suggested in Figure 4; we believe the tubes are stabilized by hemi-micelles [35–37] that sheath the surface. The superior dispersing capability of NaDDBS compared to SDS (dispersing capability,  $\leq 0.1$  mg/ml) or TX100 ( $\leq 0.5$  mg/ml) can be explained in terms of graphite-surfactant interactions, alkyl chain length, head group size and charge as pertains particularly to those molecules that lie along the surface, parallel to the tube central axis. We suspect SDS has a weaker interaction with the nanotube surface compared to NaDDBS and TX100, because it does not have a benzene ring. Indeed  $\pi$ -like stacking of the benzene rings onto the surface of graphite is believed to significantly increase the binding and surface coverage of surfactant

molecules to graphite [37]. Dextrin ( $< 0.05$  mg/ml) and DTAB ( $< 0.1$  mg/ml) also did not disperse nanotubes well because, we believe, they do not have ring moieties.

We suspect the alkyl chain part of surfactant molecules to lie flat on the graphitic tube surface, [35–37]. Most of our surfactants had alkyl chains with lengths of order 2 nm. Thus, when adsorbing onto a small diameter nanotube surface it is probably energetically favorable for the chains to lie along the length of the nanotubes rather than to bend around the circumference. This chain interaction distinguishes TX100 (8 carbon alkyl chain) from NaDDBS and SDS (both have 12 carbon alkyl chain). Longer chain lengths improve surfactant energetics, given similar ring and head groups. For example, sodium benzoate (no alkyl chain,  $\leq 0.01$  mg/ml), and NaBBS (4 carbon alkyl chain,  $< 0.1$  mg/ml) have same ring and headgroup size as NaDDBS, but performed relatively poorly because of substantially shorter alkyl chain length. On the other hand, NaOBS (8 carbon alkyl chain,  $\leq 8$  mg/ml) performed quite well. Sodium hexadecylbenzene sulfonate had a longer alkyl chain (16 carbon), but did not dissolve in water at high concentration ( $\geq 5$  wt%) at room temperature.

The different responses of NaDDBS and TX100 probably arise from head group and chain lengths. The head group of TX100 (PEO chains) is polar and larger than NaDDBS ( $\text{SO}_3^-$ ); its large size may lower its packing density compared to NaDDBS. Furthermore, the electrostatic repulsion of  $\text{SO}_3^-$  leads to charge stabilization of tubes via screened Coulomb interactions which, in analogy with colloidal particle stabilization, may be significant for solubilization in water compared to the more steric repulsion of the TX100 head group. Generally, added salt (NaCl) of greater than 25 mM induced aggregation in the NaDDBS samples. PS-PEO diblocks, which had long PEO chains as headgroup, did not stabilize nanotubes well ( $\leq 0.1$  mg/ml).

Based on our experimental, we believe that any surfactant comprised of an alkyl chain, a benzene ring moieties and either a charged or polar head group will act as a suitable dispersant for nanotubes in water. Any variation of this structure, e.g., surfactants with multiple alkyl chain tails, multiple benzene rings and several charged or polar group could very well disperse nanotubes in water.

Lastly, we investigated the relative efficacy of different sonication techniques on the dispersion of nanotubes. Tube breakage is a critical parameter; SWNTs with large lengths (e.g.,  $> 500$  nm) are often preferred because, for example, they introduce greater anisotropies into the properties of composites [30]. The standard approach is to disperse nanotubes using a

high power tip sonicator (1/8 in, 6 W, 22.5 KHz) for short time ( $\sim 1$  hour). For comparison we prepared 0.1 mg/ml of HiPCO tubes and laser-oven tubes in NaDDBS, SDS and TX100, and measured length and diameter distributions. The essential observations are summarized in Figure 5 for 0.1 mg/ml laser-oven tubes in NaDDBS. The nanotube dispersion prepared by bath sonication had very high yield of single tubes ( $\sim 90 \pm 5\%$ ), a significant fraction of which were long single tubes with lengths larger than 400nm ( $L_{\text{mean}} \sim 516 \text{ nm} \pm 286 \text{ nm}$ ), see Figure 5(a). Similar samples prepared by tip sonication (Figure 5(b)) had lower SWNT yield ( $\sim 50 \pm 4\%$ ), and  $L_{\text{mean}} \sim 267 \text{ nm} \pm 126 \text{ nm}$ . These effects were not as pronounced in HiPCO samples, because the nanotubes were already rather short.

### III. POTENTIAL APPLICATIONS

The 100X increase in nanotube solubility, and the relatively smaller amount of tube fragmentation, makes a plethora of processing schemes for SWNTs more accessible. Here is a list of some of these schemes.

1. **Preparation of composites:** There is great interest in manufacturing composite materials with large tensile and torsional strength or better thermal or electrical properties. Since our nanotubes are non-fragmented, they can readily be incorporated into any polymer matrix to increase both the tensile and torsional strength, change thermal or conducting properties. For example, one can mix nanotubes with epoxy to change the thermal property of epoxy.

2. **Self-assembly:** Now that we can prepare stable suspensions of nanotubes at high concentration, we can assemble them into 3-D crystals using graphite surfaces as template and depletion interactions or convection as the driving force.

3. **Length, chirality sorting and purification:** Since our tubes are well covered anionic surfactants in suspension, we can use electrophoresis to separate the tubes by length. The adsorbed surfactant molecules will work as "handles" and drag the tubes along the field through the electrophoresis gel. This method will also separate the tubes from impurities. We can also use the adsorption mechanism of alkyl chain of a surfactant to sort armchair nanotubes ( they are also all metallic) from zigzag or chiral tubes.

4. **Chemical and bio-sensors:** The surfactant we used to stabilize nanotube has a  $\text{SO}_3$  as head group. Nanotubes are known to respond to adsorption of single hydrogen atom [38]. Our  $\text{SO}_3$  stabilized tubes can be used as is or with slight chemical modification to detect the level of  $\text{NH}_3$  or  $\text{NH}_2$  in atmosphere and therefore, to measure pollution or minute contamination. Furthermore, we can replace  $\text{SO}_3$  group by an amine group ( $\text{NH}_2$ ). Nanotubes with amine surface group can easily bind to different kind proteins and act as bio-sensors.

5. **Controlled deposition on surfaces:** Since our tubes are well covered by a negatively charged surfactants, we can effectively deposit the tubes on a positively charged surface (e.g., positively charged silicon wafer) at any specific location. This capabilities can have wide use in circuit design with nanotubes. After deposition, the surfactants on the tube can readily be vaporized by baking the resultant wafer at  $180^\circ \text{C}$ .

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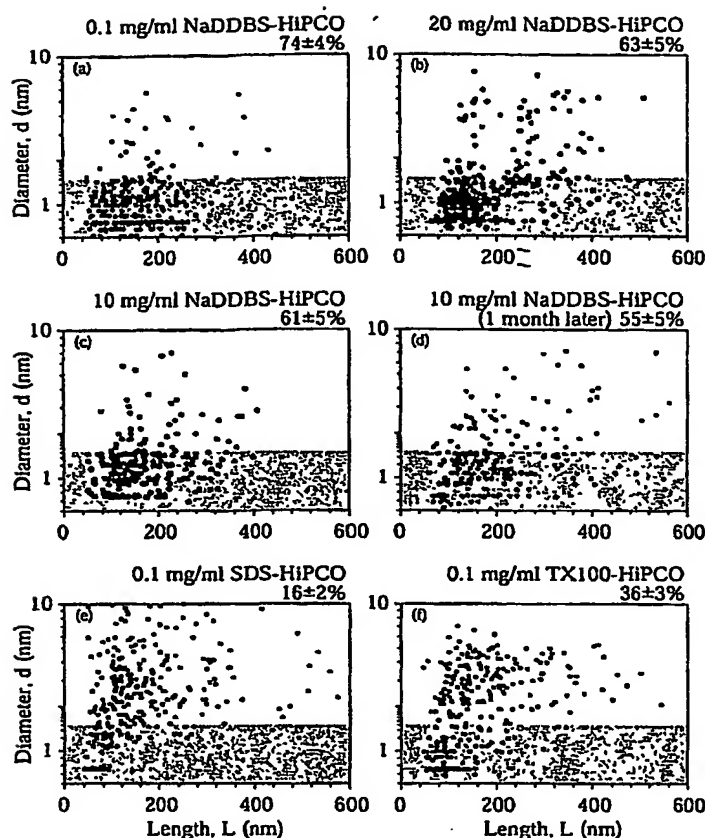


FIG. 3: Length and diameter distribution of HiPCO tubes, obtained from AFM images, after dispersed by bath sonicator and stabilized by 3 different surfactants. When the original suspension concentration was greater than 0.1 mg/ml, the dispersions were rapidly diluted to 0.1 mg/ml, and then spread over a silicon wafer for the AFM distribution measurements. Note, the contributions of tubes whose lengths were less than 50 nm are not reflected in these distributions because of the lateral resolution of our measurements made it difficult for us to unambiguously detect them. (a) The fraction of single tubes in a NaDDBS-HiPCO solution prepared at 0.1 mg/ml was  $\sim 74 \pm 5\%$ . (b) We obtained  $\sim 63 \pm 5\%$  single tubes when we prepared NaDDBS-HiPCO solution at 20 mg/ml. (c) A NaDDBS-HiPCO solution prepared at 10 mg/ml had  $\sim 61 \pm 5\%$  single tubes. (d) The distribution did not change appreciably when we looked at the sample after a month ( $\sim 55 \pm 5\%$  single tubes). When we prepared 0.1 mg/ml HiPCO solution with SDS or TritonX-100 surfactant, the fraction of single tubes were  $16 \pm 2\%$  (d) and  $36 \pm 3\%$  (e), respectively.

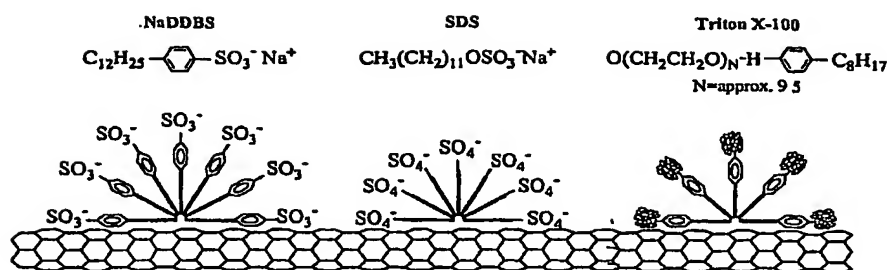


FIG. 4: A schematic representation of how surfactant may adsorb onto the nanotube surface. We speculate that the alkyl chain groups of a surfactant molecule adsorb flat along the length of the tube instead of the diameter. NaDDBS and TX100 disperse the tubes better than SDS because of their benzene rings. NaDDBS disperses better than TX100 because of the head group and slightly longer alkyl chain (see text).

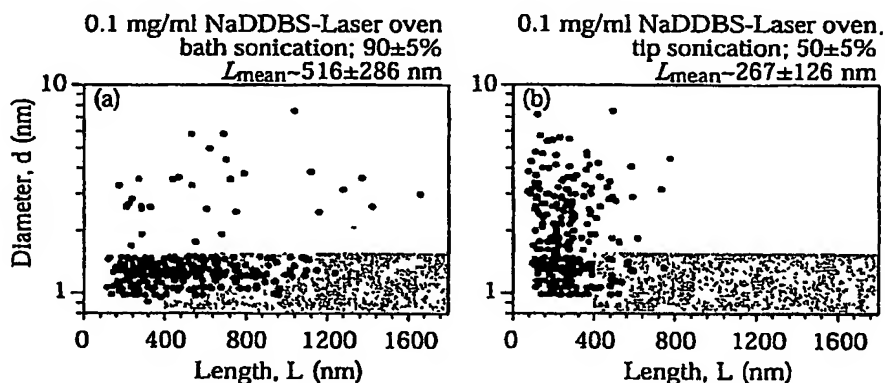


FIG. 5: Length and diameter distribution of 0.1 mg/ml laser-oven single-walled nanotube suspension dispersed by tip and bath sonicators and stabilized by NaDDBS. (a) The low-power bath sonication scheme made high yield single tubes ( $90 \pm 5\%$ ) and left many single tubes with lengths larger than 400 nm.  $L_{\text{mean}}$  was  $\sim 516 \pm 286$  nm. (b) The tip-sonication technique gave significantly lower yield ( $50 \pm 5\%$ ) and also fragmented the tubes. We observe only a few nanotubes with lengths larger than 400 nm;  $L_{\text{mean}}$  was  $\sim 267 \pm 126$  nm.